

# PATENT SPECIFICATION

(11) 1 407 659

1 407 659

- (21) Application No. 11450/73 (22) Filed 9 March 1973  
 (31) Convention Application No. 244264 (32) Filed 14 April 1972 in  
 (33) United States of America (US)  
 (44) Complete Specification published 24 Sept. 1975  
 (51) INT CL<sup>2</sup> A61K 7/11  
 (52) Index at acceptance

C3P 102 7D2A1 7K8 7K9 8D1A 8D1B 8D1X 8D2A  
 8D2B2 8D4 8K7 8K8 8K9 9D1A1 9K7 9K8 D3B  
 E2 P1D P1E1 P3 PC13A PC14A PC14B PC15  
 PC16A PC17 PC20B PC6A PC9

A5B 774  
 C4X 11

- (72) Inventors ALBERT L. MICCHELLI, GERARD J. LEGATO  
 STUART H. GANSLAW and  
 LAWRENCE D. SCHULER



## (54) HAIR FIXING COMPOSITION

(71) We, NATIONAL STARCH AND CHEMICAL CORPORATION, a corporation organised and existing under and by virtue of the laws of the State of Delaware, United States of America, of 750 Third Avenue, New York, New York 10017, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a hair fixing composition containing a film forming polymeric binder.

In order to be highly effective in hair fixing compositions such as aerosol hair sprays and hair setting lotions, the film forming polymeric binders utilized therein as well as the films derived therefrom must meet a rigid set of requirements. Thus, the binders used in such formulations should be soluble or dispersible in, open, anhydrous organic solvents, yet the films cast from such hair fixing formulations should, ordinarily, either be water soluble or water dispersible in order to facilitate their easy removal from the user's hair. As is readily visualized, this is an unusual combination of properties which is further complicated by the requirement that the binder used in such formulations be completely compatible with the solvents and/or propellants ordinarily employed therein. Furthermore, the binders used should show little or no tendency to interact with the perfumes or other optional ingredients utilized in hair fixing formulations.

In addition, the films cast from either aqueous or organic solvent solutions of these binders should be flexible and should simultaneously exhibit sufficient strength and elastic-

ity; they should exhibit good adhesion to hair so as to avoid the occurrence of dusting or flaking when the hair is subjected to varying stresses; they should readily allow the hair to be recombined; they should maintain a non-tacky state despite humid conditions; they should be clear, transparent and glossy and should possess good antistatic properties; and they should be easily removable by the use of water and/or soap or shampoo.

Needless to say, many polymeric systems have been utilized in an attempt to meet these stringent requirements. Among these are included: polyvinylpyrrolidone, copolymers of N-vinyl pyrrolidone with vinyl acetate, 5,5' - dimethyl hydantoinformaldehyde resins, and copolymers of methyl vinyl ethers and maleic acid half esters. Though each of these polymer systems has met at least some of the above cited requirements, none has exhibited all of these requirements to an optimum degree.

We have now discovered a class of polymers, hereinafter described, which are particularly useful as the film forming binder component of hair fixing compositions. Particularly significant are the good solubility and compatibility characteristics exhibited by these binders. Thus, for example, they display a good degree of solubility in the organic solvents typically used in aerosol hair sprays as well as in the aqueous solvent systems typically utilized in wave set lotions. In addition, they exhibit good compatibility with the hydrocarbon propellants typically used in aerosol hair sprays. Furthermore, if neutralization of these resins is desired by the practitioner, the lower levels of neutralization that can be used help to ensure the deposition, onto the hair, of films having a minimal

45

50

55

60

65

70

75

80

degree of water sensitivity which, although they are readily removable by washing, provide a greater degree of holding power and thereby enable the thus treated hair to retain its shape and body.

Thus, the present invention provides a hair fixing composition comprising a solution or dispersion in a solvent selected from an organic solvent, water and a mixture of an organic solvent and water, of an interpolymer containing

(1) 30—60% by weight of moieties desired from a comonomer selected from N-substituted alkylacrylamides and N-substituted alkyl methacrylamides wherein the alkyl group thereof contains from 2 to 12 carbon atoms,

(2) from 10—20% by weight of moieties derived from an acidic copolymerizable comonomer having at least one available carboxylic acid group, and

(3) 20—55% by weight of moieties derived from at least one copolymerizable comonomer selected from  $C_1$ — $C_{12}$  alkyl acrylates and methacrylates, hydroxyalkyl acrylates and methacrylates, primary, secondary, tertiary and quaternary amine-substituted acrylates and methacrylates, vinyl acetate, vinyl propionate, diacetone acrylamide, styrene and alpha-methyl styrene, said percentages totaling 100%; said interpolymer being present in an amount of 0.25 to 7% by weight of said composition.

Among the applicable N-substituted acrylamides and methacrylamides from which the interpolymer used in the present invention may be formed are included N-ethyl acrylamide, N-tertiary-butyl acrylamide, N-n-octyl acrylamide, N-tertiary-octyl acrylamide, N-decyl acrylamide, N-dodecyl acrylamide, as well as the corresponding methacrylamides.

The following list of monomers are representative of the applicable acidic film forming comonomers which contain at least one available carboxyl group: acrylic acid, methacrylic acid, crotonic acid, itaconic acid, maleic acid, fumaric acid and the  $C_1$ — $C_4$  alkyl half esters of maleic and fumaric acids such, for example, as methyl hydrogen maleate and butyl hydrogen fumarate as well as any other acidic monomers which are capable of being copolymerized with the particular comonomers whose use is desired by the practitioner.

The acidic comonomers make it possible for the resultant copolymer to be neutralized by reaction with an appropriate base in order that it may ultimately exhibit the requisite water solubility. These acidic comonomers may be neutralized prior to their being incorporated into the ultimate hair fixing formulation thus permitting these formulations to be removed from the hair merely by rinsing with water. However, if such copolymers are not preneutralized in this manner, removal may still be readily effected by the applica-

tion of an alkaline aqueous solution, for example, soap and water. It should be noted that for purposes of this invention the term "water solubility" is meant to include both water solubility in its usual meaning as well as water dispersibility wherein the resulting films are sufficiently hydrated and softened by contact with water so as to be easily removed from the hair by the application of water and either soap or a shampoo.

The other comonomer or comonomers is (are) present in order to modify certain properties of the polymeric binder, for example water solubility, hardness and antistatic properties. These further comonomers are the acrylic and methacrylic acid esters of aliphatic alcohols having from 1—12 carbon atoms e.g. methyl, ethyl, propyl, butyl, octyl and lauryl alcohols; hydroxyalkyl esters of acrylic and methacrylic acids e.g. as hydroxypropyl acrylate and methacrylate, hydroxybutyl acrylate and methacrylate, hydroxystearyl acrylate and methacrylate and hydroxyethyl acrylate and methacrylate; primary, secondary, tertiary and quaternary amine-substituted esters of acrylic and methacrylic acids e.g. amino-ethyl methacrylate, N,N' - dimethylaminoethyl methacrylate, N-tertiary-butyl aminoethyl methacrylate and the quaternization product of dimethylaminoethyl methacrylate and dimethyl sulfate and diethyl sulfate, diacetone acrylamide, vinyl acetate; vinyl propionate; styrene; and alphanemethyl styrene.

As for the actual preparation of these polymeric film forming binders, there may be employed any of the usual vinyl polymerization methods which are well known to those skilled in the art and which are particularly suited for the polymer whose preparation is desired. Thus, the polymers may be prepared by means of free radical initiated processes utilizing bulk, suspension, solution, or emulsion polymerization techniques. The polymers may, if desired, be converted into relatively large particles known as beads or pearls by dispersing the solution polymerized polymer in water and thereafter driving off the solvent followed by separating and drying the particles.

It should be noted that the polymer binders used in this invention may be partially neutralized prior to their being incorporated into the ultimate hair fixing formulation thus permitting them to be removed from the hair merely by rinsing with water. This may be accomplished by reacting the polymer, in the form of a solution in an organic solvent, with or without added water, with a concentration of an alkaline reagent which is equivalent on a molar basis to a minimum of about 50% of the available carboxyl groups present on the polymer. Applicable neutralizing agents which may be utilized in this manner include: sodium and potassium hydroxide;

ammonia; primary, secondary and tertiary amines; alkanolamines; and, hydroxyamines such as 2 - amino - 2 - methyl - propanol and 2 - amino - 2 - methyl - 1,3 - propanediol. However, if such polymers are not pre-neutralized in this manner, their eventual removal may still be readily effected by the application of weak alkaline aqueous solution, e.g., soap and water. If the polymer binders are sufficiently neutralized, it should be possible to use water by itself as the solvent. Example 12 below describes a wave setting lotion which does not contain organic solvent.

In utilizing the above-described polymeric binders in the preparation of aerosol hair sprays, the other essential ingredients which must be admixed therewith are a solvent and a propellant, although in some instances the propellant will serve both the latter functions. The preferred solvents are alcohols such as ethanol and isopropanol. In addition to their solubility properties, the prime advantages of these solvents are their ability to dry quickly, their minimal effect on the metal containers ordinarily utilized for these pressurized aerosol formulations and their accepted use in cosmetic applications. Other solvents which may be used include methylene chloride and 1,1,1 - trichloroethane.

Various types of aerosol propellants are well known to those skilled in the art. Thus, the commonly used propellants include trichlorofluoromethane, dichlorodifluoromethane, isobutane and propane, as well as mixtures of the latter propellants. These propellants are readily compatible with the binder-solvent solutions utilized in this invention.

In general, the method for preparing the hair spray formulations of this invention merely involves dissolving or diluting the polymer in the selected solvents, adding any modifying agents whose presence may be desired, and thereupon combining the resulting solution with the selected aerosol propellant.

Thus, it may be noted that the hair spray formulations of this invention will in most cases contain at least three essential components. The first of the latter components will be what may be termed as the active ingredient comprising one or more of the above-described interpolymers which serves as the binder for the formulation. Secondly, there will be one or more solvents which serve as vehicles for the binder. And, finally, there is the propellant which serves to effect the discharge of the aforescribed binder and vehicle from the container wherein the formulation is packaged. Water is not ordinarily present, but may be included in some formulations.

With regard to proportions, the final hair spray formulations contain the polymeric binder in a concentration ranging from 0.25

to 7%, by weight; while its amounts of the other components are typically as follows: the solvent in a concentration ranging from 8 to 90%, by weight; and, the propellant concentration ranging from 10 to 85%, by weight. The proportions of solvent and propellant just quoted should, however, be considered as being merely illustrative inasmuch as it may well be possible to prepare operable formulations having concentrations of these components which fall outside these ranges.

In addition, it should be noted that the film forming polymers used in this invention are equally effective when utilized in hair setting lotions, which usually consist of a solution (or dispersion) of the polymer in a suitable organic solvent, such as alcohol, together with water, or in water alone. Such lotions may be directly applied to the hair or they may be sprayed thereon utilizing conventional spray nozzles. The application of such lotions may take place prior to, during, or after the desired hair style has been achieved.

The latter hair lotions are prepared by merely admixing the film forming polymer with the selected solvent, such solvents usually comprising a mixture, with water, of an alcohol such as ethanol or isopropanol. With regard to proportions, the lotions, like the other hair fixing compositions of this invention, contain from 0.25 to 7%, by weight, of the polymeric binder, while any desired ratio of alcohol to water in the solvent system may be utilized therein. An all alcohol or all water system may also be used in some cases.

Optional additives may be incorporated into the hair fixing compositions of this invention in order to modify certain properties thereof. Among these additives may be included: plasticizers such as glycols, phthalate esters and glycerine; silicones; emollients, lubricants and penetrants such as lanolin compounds, protein hydrolyzates and other protein derivatives, ethylene oxide adducts, and polyoxyethylene cholesterol; U.V. absorbers; dyes and other colorants; and, perfumes. The polymeric binders used in this invention, at least in preferred cases, show little or no tendency to chemically interact with such additives.

The preferred hair fixing compositions of this invention exhibit to a remarkable degree the characteristics required of such a product. Their films are transparent, glossy, flexible, and strong. They possess good antistatic properties, adhere well to hair, are easily removed by soapy water or shampoos, allow the hair to be readily combed, do not yellow on ageing, do not become tacky when exposed to high humidities, and have excellent curl retention under high humidity conditions.

In the following examples, which further

illustrate the invention, all parts given are by weight unless otherwise indicated.

#### Examples 1—5

These examples illustrate a method for the preparation of typical polymers applicable for use in the hair fixing compositions of this invention.

A reaction vessel fitted with a condenser and means for mechanical agitation was charged with 50 parts N-tertiary-octyl acrylamide, 15 parts acrylic acid, 35 parts methyl acrylate 1.0 part benzoyl peroxide and 100 parts of ethanol. The contents were heated

to the reflux temperature of the system and held there for a period of six hours whereupon an additional 1.0 part of benzoyl peroxide was added thereto. The system was then held at reflux for an additional four hours whereafter the reaction was cooled to 30°C and the polymer #1 recovered.

Additional polymers applicable for use in the hair fixing formulations of this invention were also prepared by means of the above-described procedure; the reagents and the concentrations in which they were used to prepare the respective polymers being set forth in the following table:

30	Comonomers	Parts Polymer (Example #)			
		2	3*	4*	5*
	N-tert.-octyl methacrylamide	—	—	40	—
	N-tert.-octyl acrylamide	—	30	—	—
	N-tert.-butyl acrylamide	55	—	—	35
	Acrylic Acid	10	—	—	—
35	Methacrylic Acid	—	15	—	10
	Crotonic Acid	—	—	10	—
	Methyl Methacrylate	—	20	—	40
	Methyl Acrylate	—	15	25	—
	Tert.-Butyl Methacrylate	35	—	—	—
40	Hydroxypropyl Methacrylate	—	10	10	—
	Hydroxypropyl Acrylate	—	—	—	5
	Tert.-butyl Aminoethyl Methacrylate	—	—	—	10
	Dimethyl Aminoethyl Methacrylate	—	10	—	—
	Diacetone Acrylamide	—	—	15	—

\*Azobisisobutyronitrile substituted for benzoyl peroxide as free radical initiator.

#### Examples 6—8

These examples illustrate a further method of polymerization applicable to the preparation of binders for use in the invention.

A reaction vessel fitted with a condenser and means for mechanical agitation was charged with 100 parts ethanol and 1.0 part benzoyl peroxide. Thereafter the vessel was charged with 25% of a monomer mix containing 40 parts N-tertiary-octyl acrylamide, 15 parts acrylic acid, 35 parts methyl methacrylate, 5 parts hydroxypropyl acrylate and 5 parts tertiary-butyl aminoethyl methacrylate. The system was heated to its reflux temperature whereupon the remainder of the monomer mix was added over a period of 4 hours. Upon completion of the monomer addition, an additional 1.0 parts of benzoyl peroxide was added and the reaction held at reflux for a further 4 hours. The system was cooled and polymer #6 recovered therefrom.

Additional copolymers applicable for use in the hair fixing formulations of this invention were also prepared by the above-described procedure; the reagents and the concentrations in which they were used to prepare

the respective polymers being set forth in the following table:

Comonomers	Parts Polymer (Example #)	
	7	8
N-dodecyl Acrylamide	60	50
Acrylic Acid	20	—
Maleic Acid	—	15
Methyl Methacrylate	20	—
Methyl Acrylate	—	10
Hydroxypropyl Acrylate	—	10
Styrene	—	15

#### Examples 9—11

These examples illustrate the preparation of aerosol hair spray formulations typical of the compositions of this invention.

A solution of the desired polymer in anhydrous ethanol was prepared and subsequently introduced into an aerosol container which had been charged with the desired propellant to an internal pressure of 30 lbs. per square inch gauge. The various modifying agents were added to the polymer-alcohol solutions prior to their introduction into the propellant-charged aerosol container.

The reagents and the concentrations utilized for preparing the various aerosol hair sprays are set forth in the following table:

		Parts Aerosol Spray(Example #)		
		9	10	11
5	Polymer #1 (dried)	0.250	7.000	—
	Polymer #6 (dried)	—	—	0.50
	2-amino-2 methyl propanol	0.042	1.750	—
	Perfume oil	0.10	0.10	0.10
10	Polymethylpolysiloxane	0.250	—	—
	Ethoxylated lanolin oil	—	—	0.50
	Hydrolyzed protein	—	0.70	—
	Anhydrous ethanol	49.358	10.450	63.90
15	A 40:60 propellant mixture of dichloro- difluoromethane and trichlorofluoro- methane	50.0	80.00	—
	A 45:45:10 propellant mixture of tri- chlorofluoromethane: dichlorodi- fluoromethane: isobutene	—	—	35.00
20	% of available carboxylic acid groups neutralized in polymer	55	81	—

It was noted that each of the resulting hair sprays was completely compatible. When utilized, each of the sprays deposited a film which was characterized by its clarity, gloss and flexibility. Each film retained its original non-tacky state and was resistant to the build-up of electrostatic charge. It served to hold the desired hair style in place while also allowing for its recombining. Of great significance was the fact that it was readily removed

from the hair by the use of an aqueous soap solution.

#### Examples 12—14

These examples illustrate the preparation of wave setting lotions typical of the compositions of this invention.

The lotions noted in the following table were prepared by charging the specified ingredients into a reaction vessel equipped with means for mechanical agitation.

		Parts Wave Set Lotion (Example #)		
		12	13	14
45	Polymer #1 (dried)	0.500	3.000	7.000
	2-amino-2 methyl propanol	0.156	0.750	1.300
	Anhydrous ethanol	—	46.25	91.70
	Water	99.344	50.000	—
50	% of available carboxylic acid groups neutralized in polymer	100	80	60

When utilized, each of these wave setting lotions deposited a clear, glossy, flexible film which was readily removed from the hair by a thorough washing with water.

#### WHAT WE CLAIM IS:—

1. A hair fixing composition comprising a solution or dispersion in a solvent selected from an organic solvent, water and a mixture of an organic solvent and water, of an interpolymers containing

(1) 30—60% by weight of moieties derived from a comonomer selected from N-substituted alkyl acrylamides and N-substituted alkyl methacrylamides wherein the alkyl group thereof contains from 2 to 12 carbon atoms,

(2) from 10—20% by weight of moieties

derived from an acidic copolymerizable comonomer having at least one available carboxylic acid group, and

(3) 20—55% by weight of moieties derived from at least one copolymerizable comonomer selected from C<sub>1</sub>—C<sub>12</sub> alkyl acrylates and methacrylates, hydroxyalkyl acrylates and methacrylates, primary, secondary, tertiary and quaternary amine-substituted acrylates and methacrylates, vinyl acetate, vinyl propionate, diacetone acrylamide, styrene and alpha-methyl styrene, said percentages totaling 100%; said interpolymers being present in an amount of 0.25 to 7% by weight of said composition.

2. A hair fixing composition according to Claim 1, wherein said interpolymers contains

moieties derived from N-tertiary-octyl acrylamide and acrylic acid.

- 5 3. A hair fixing composition according to Claim 1 or Claim 2, wherein the composition also contains a neutralizing agent.

- 10 4. A hair fixing composition according to any preceding claim, wherein the interpolymer is dissolved in an organic solvent and the composition also contains an aerosol propellant therefor.

- 5 5. A hair fixing composition according to any preceding claim, wherein the interpolymer is substantially as described in any one of Examples 1—8 herein.

- 15 6. A process for fixing hair, characterized

by applying to the hair a hair fixing composition according to any preceding claim.

7. An aerosol hair spray formulation, according to Claim 4 and substantially as described in any one of Examples 9—11 herein.

8. A wave setting lotion, according to Claim 1 and substantially as described in any one of Examples 12—14 herein.

20

TREGEAR, THIEMANN & BLEACH,  
Chartered Patent Agents,  
Melbourne House,  
Aldwych,  
London, W.C.2.,  
Agents for the Applicant(s).

Printed for Her Majesty's Stationery Office, by the Courier Press, Leamington Spa, 1975.  
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from  
which copies may be obtained.